Characteristics of high quality ZnO thin films deposited by pulsed laser deposition

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(Received 6 July 1994; accepted for publication 5 October 1994)

Thin films of ZnO have been deposited on glass and silicon substrates by the pulsed laser deposition technique employing a KrF laser (λ=248 nm). The influence of the deposition parameters, such as substrate temperature, oxygen pressure, and laser fluence on the properties of the grown films, has been studied. All the films grown over a rather wide range of deposition conditions were found to be optically transparent, electrically conductive, and *c*-axis oriented, with the full width at half-maximum (FWHM) of the (002) x-ray reflection line being very often less than 0.25°. Under optimized laser fluence and oxygen pressure conditions, highly *c*-axis oriented films having a FWHM value less than 0.15° and optical transmittance around 85% in the visible region of the spectrum have been grown at a substrate temperature of only 350 °C. These are among the best properties yet reported for ZnO films grown by any technique at such a low temperature. © *1994 American Institute of Physics.*

There has recently been a surge of interest in the growth of high quality thin films of ZnO,[1–5] an optical transparent (energy band gap, E_g=3.26 eV) *n*-type semiconductor exhibiting, when *c*-axis oriented, large piezoelectric and piezooptic properties.[6] However, for the full exploitation of the attractive properties of ZnO thin films in sensors or optically active devices, there is a stringent need to deposit high quality *c*-axis oriented layers at modest substrate temperatures, usually below 450 °C.

Almost all of the major deposition techniques such as sputtering,[7,8] chemical vapor deposition,[9] sol-gel,[10] chemical spraying,[11] electron plasma sputtering,[12] or ion-beam assisted deposition[5,13] have been employed for the growth of ZnO films. As the pulsed laser deposition (PLD) method has been recognized to offer the potential of growing high quality thin films at relatively lower substrate temperatures than other techniques,[14,15] its use in growing ZnO films has been studied.[16–20]

In our previous papers,[19,20] we have shown that in the vast majority of cases higher quality films can be grown when employing a KrF laser (λ=248 nm) for ablation rather than a frequency doubled: Nd:YAG laser (λ=532 nm). In this letter we show that under optimized deposition conditions films can be grown having a full width at half-maximum (FWHM) value of the (002) x-ray diffraction (XRD) line a factor of 4 smaller than the previously published results using PLD[18] and among the best reported so far by any technique.[21,24]

Cylindrical ZnO targets of 99.9% purity were fabricated in-house and ablated by a KrF laser within our PLD setup, which has been described in detail elsewhere.[19,20,25] A diaphragm placed in the beam path ensured that only the central uniform (±5%) part of the laser beam was used and that the ablation spot-size remained unchanged for all the irradiation conditions employed. The incident laser fluence was adjusted within the 0.5–5 J/cm^2 range by varying the energy contained in each laser pulse. The deposition cell was initially evacuated to pressures in the low 10^{-6} or 10^{-7} Torr range, then purged, re-evacuated, and finally filled with oxygen (99.999% purity) at working pressures of between 5×10^{-6} and 2×10^{-2} Torr. The films were deposited on either (100) silicon or Corning glass substrates placed on a heater situated 4 cm in front of the target. The substrates were cleaned using acetone, alcohol, and de-ionized water, and blown dry with N_2 to ensure good reproducibility of the film properties.

The crystalline structure of the grown ZnO films was investigated by XRD. The CU K_α source used emits three lines, $K_{\alpha1}$=0.154 060 nm and $K_{\alpha2}$=0.154 439 nm (intensity half that of K_α) as well as K_β=0.139 222 nm, which was removed by placing a filter in the x-ray beam. In calculations we used a weighted average value for a hypothetical line K_α with a wavelength of 0.154 186 nm. The thickness and refractive index value of the layers at 632 nm were measured by ellipsometry, while the surface morphology and cross-sectional structure of fractured films were investigated using a scanning electron microscope (SEM). The optical transmittance of the films deposited on Corning glass substrates was measured in the 300–900 nm range with a double beam spectrophotometer and the electrical resistivity by the van der Pauw method.

All the layers deposited at room temperature were found to be essentially amorphous, with no sharp XRD reflection lines being present, and exhibited a matt surface. For substrate temperatures from 200 up to 500 °C, all the grown films were found to be *c*-axis oriented, exhibiting only the (002) and (004) XRD lines. It is worth mentioning that for a wide range of laser fluences and oxygen partial pressures employed, the FWHM of the (002) line was typically less than 0.25°, indicating a high quality crystalline structure. Although there is, in terms of XRD linewidths, a beneficial effect associated with the increase of the substrate temperature from 150 to 350 °C, this tendency is reversed for tem-

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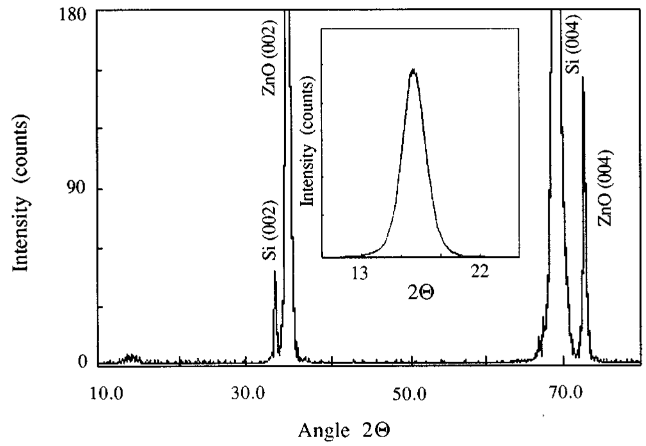

FIG. 1. XRD spectrum of a ZnO thin film deposited under optimized conditions. The rocking curve recorded for the (002) line is shown in the insert.

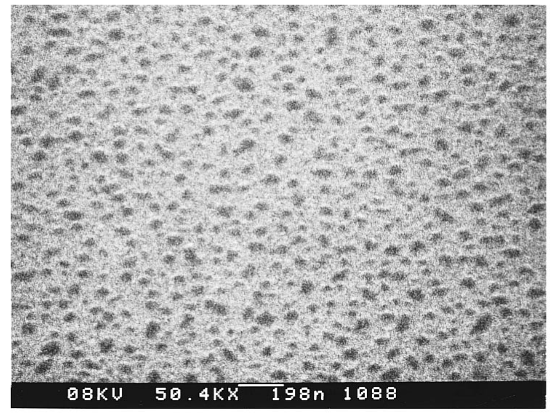

FIG. 2. SEM micrograph of the film surface recorded at an incidence angle of 45°.

peratures higher than 400 °C. Consequently, most of the films in this study were grown at 350 °C.

Investigations of the effect of different oxygen partial pressures showed that the best quality films could be obtained in the higher pressure range, i.e., around $1–4\times10^{-3}$ Torr. This result is quite different from that obtained when growing ZnO thin films using a frequency doubled Nd:YAG laser.[19,20] The electrical resistivity of the films was strongly affected by the oxygen deposition pressure, increasing from $7–9\times10^{-3}$ Ω cm for films deposited at 2×10^{-5} Torr, to $5–8\times10^{-2}$ Ω cm for those deposited at 2×10^{-3} Torr. This behavior can be easily understood taking into account that the electrical conductivity of ZnO is controlled by Zn interstitials or O vacancies.

Refractive index values around 1.98 and good crystalline properties were recorded for all the films grown at laser fluences in the 1.5–2.5 J/cm^2 range, for substrate temperatures around 350 °C and oxygen partial pressures in the low 10^{-3} Torr range. For fluence values outside this range, broader XRD lines and lower refractive indices were found. To summarize, these studies have shown that the best conditions for PLD of ZnO thin films necessitate substrate temperatures between 300 and 350 °C, oxygen partial pressures from $1–2\times10^{-3}$ Torr and laser fluences around 2 J/cm^2. Within this range, the FWHM of the (002) XRD line is always below 0.18° and the transparency above 85% in the visible region of the spectrum.

In Fig. 1, the XRD spectrum recorded for a ZnO film grown with a fluence of 2.1 J/cm^2, substrate temperature of 350 °C and oxygen pressure of 2×10^{-3} Torr (hereafter called the optimized conditions), is shown. Only the (002) and (004) XRD lines are present along with the (100)Si lines of the substrate. The c-axis lattice constant, estimated from the peak position of the (002) line is 0.519 65 nm, as compared to the c-axis lattice value of 0.520 66 nm recorded for ZnO powder.[6] The tensile macrostrain corresponding to this value is only 1.9×10^{-3}. The FWHM of the (002) reflection line, corrected for the instrumental broadening as derived from the width of the Si (002) peak, is 0.13°, one of the lowest values yet reported in the literature.[22–24,26] Apart from a small peak situated at around 10°, most likely due to the presence of a very thin amorphous transitional layer situated between the Si substrate and the grown ZnO film, no other XRD line is present. The rocking curve measured for the (002) line, keeping 2Θ fixed at 34.51° is shown as an insert in Fig. 1. The top of the resulting curve is situated at 16.99°, while the FWHM is only 2.07°, a value which compares very favorably with those usually reported in the 2.5–3.0° range.[12,23] The standard deviation of the rocking curve is $\sigma=0.62°$, a value which was previously measured only for the highest quality ZnO films[4] and those deposited on sapphire substrates.[24]

SEM investigations, when performed at normal incidence, revealed very smooth surfaces for the deposited films. At 45° incidence, some contrast corresponding to the presence of crystalline grains can be seen, as shown in Fig. 2. Minimization of the occurrence of droplet formation, a general drawback of the PLD method, was assisted by the use of the ultraviolet laser. Since the optical absorption of 248 nm radiation is very high in ZnO, typically above 3×10^5 cm^{-1} at room temperature,[6] a steep thermal gradient is induced within the target with the maximum temperature situated at the surface.[26] The fractured ZnO film surfaces reveal a dense, columnar structure as can be seen in Fig. 3. Interestingly, such a structure is quite similar to that of the transitional

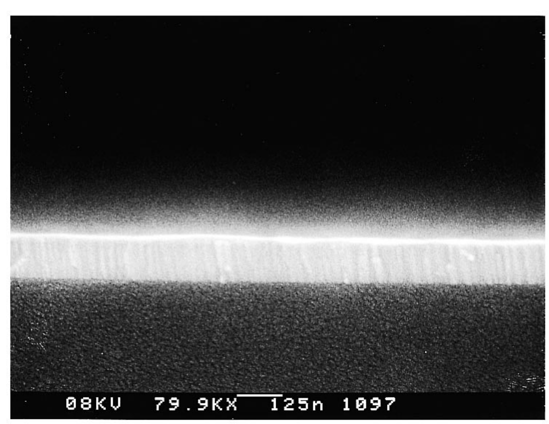

FIG. 3. SEM micrograph of a ZnO fractured film showing a dense columnar structure.

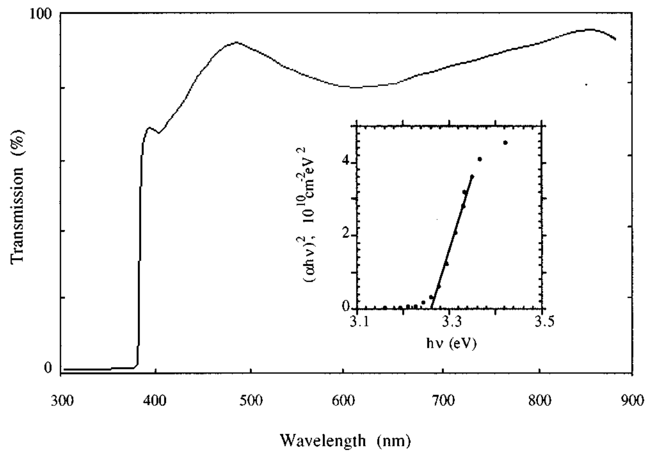

FIG. 4. Optical transmittance of a ZnO film grown under the same conditions as those used for the film measured in Fig. 1. The insert shows the Tauc plot.

zone T of the Thornton model[27] exhibited by sputtered ZnO films.[23]

The transmittance spectrum of a ZnO film grown under similar deposition conditions to those of the film presented in Fig. 1, but on a Corning glass substrate is presented in Fig. 4. An average transmittance of 85% in the visible region with a steep falloff at 380 nm, characteristics of high quality ZnO films,[28–30] can be seen. From the plot of the absorption coefficient versus wavelength in the region of high optical absorption (Tauc plot[31] shown as an insert in Fig. 4), an optical band-gap energy of 3.26 eV was estimated, a value identical to that recorded for single crystal ZnO.[6] From the recorded transmittance spectra and following the model of Manifacier *et al.*,[32] a film thickness of 300 nm (corresponding to a growth rate of 0.1 nm/pulse) a refractive index $n=1.97 \pm 0.03$ and an extinction coefficient, $k=6\times10^{-3}$ at 600 nm have been estimated. Similar values for the refractive index ($n=1.98$–1.99) and thicknesses (290–295 nm) have been measured by ellipsometry for films deposited under identical conditions on Si substrates.

In conclusion, some of the best quality films in terms of crystalline structure and optical properties have been grown at substrate temperatures around 350 °C employing the PLD method. By studying the effect of deposition parameters on the film structure, optimized conditions for growth have been identified. Under such conditions, c-axis oriented ZnO films having a FWHM value of the (002) XRD reflection line less than 0.15°, electrical resistivities around $5\times10^{-2}\ \Omega$ cm and optical transmittance higher than 85% in the visible region of the spectrum were obtained. The surface morphology was featureless and the fractured surface exhibited a dense, columnar structure. The refractive index was around 1.98 and the $E_g=3.26$ eV, values characteristic of very high quality ZnO thin films.

This work was supported by the Engineering and Physical Science Research Council (Contract No. GR/H67133) with additional financing from the joint Netherlands Organization for Scientific Research (NWO) and British Council programme (No. JRP006). The authors wish to thank Professor M. Green for the use of the ellipsometer, Dr. S. Best for the use of the spectrophotometer, and D. Craciun for analysis of the optical data.

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